

**PRODUCTION AND CHARACTERIZATION OF PYROLYTIC
PRODUCTS OBTAINED FROM PYROLYSIS OF SIMAL COTTON**

SEED (*Bombax malabarica*)

A Thesis submitted in partial fulfillment of the requirements for

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Submitted by

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CERTIFICATE

This is to certify that the work in this report entitled “**Production and characterization of pyrolytic products obtained from pyrolysis of simal cotton seed (*Bombax malabarica*)**.” submitted by Ravi (Roll Number 710CH1114) in partial fulfillment of the requirements of the prescribed curriculum for M-tech Dual Degree in Chemical Engineering Session 2014-2015 in the Department of Chemical Engineering, National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the report is his bona fide work.

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ABSTRACT

In this work, simal cotton seed (*Bombax malabarica*) has been chosen as the material of interest and serves as biomass. The simal cotton seeds were subjected to pyrolysis in a semi batch reactor, the characteristics and yield of the liquid and solid product were determined. The main objective of this work was to determine the possibility of finding a product using various methods so that it may serve as a fuel or may be used as a valuable product. Pyrolysis experiments were carried out in the temperature range of 450°C to 700°C at the heating rate of 20°C min⁻¹. A maximum liquid product yield of 58.06% (by weight) was obtained which has the calorific value of 6678.5416 Kcal/kg. The thermal degradation of the simal cotton seed was studied in an inert atmosphere by Thermogravimetric Analyzer (TGA) and its kinetic study was also done using various model fitting and model free methods. The pyrolytic oil and the pyrolytic char obtained was characterized using methods like FTIR, GC/MS, SEM-EDX and its physical properties were determined using standard procedure prescribed in literature.

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NOMENCLATURE

GC-MS	Gas chromatography mass spectroscopy
FTIR	Fourier transform infrared spectroscopy
TGA	Thermogravimetric analysis
TG	Thermogravimetry
DTG	Differential Thermogravimetry
GCV	Gross calorific value

Chapter 1

(INTRODUCTION)

1. Introduction

The basic needs of human beings for their survival are food, clothing and shelter but all of them require energy for their synthesis, production or manufacture. So we can say that without energy we are not able to fulfil our basic needs of life. From thousands of years fossil fuel were the primary source for energy production. But due to the rapid growth of population and urbanization the fossil fuels are on the verge of depletion. So we require an alternate energy source to fulfil our needs. Biomass is estimated to contribute with 10-14 % to the world's total energy supply [1]. Beside this problem, our critical environmental conditions is a big issue of concern these days. As we all are aware that combustion of fossil fuels releases CO₂ in the atmosphere which is a Greenhouse gas which causes Global Warming. So it has become a necessity to find an alternative source of energy which is renewable as well as environment friendly. Scientists and Researchers are working for years to find a suitable and alternative source of fuel. They have come up with various sources of energy such as solar energy, wind energy, tidal energy, energy derived from biomass etc. Out of these, energy derived from Biomass is used commercially while the others have a little commercial importance.

Biomass refers to almost any organic matter derived from plants or animals and is renewable over time. More simply we can say that biomass is stored energy. It includes the product, by-product, residues and wastes from agricultural, forestry, industrial and municipal wastes. Burning of biomass does not add any extra CO₂ to the environment. It absorbs atmospheric CO₂ while it grows and returns it back to the atmosphere when it is consumed.

Biomass has been found to be a source of variety of fuels and useful chemicals. Its thermal pyrolysis produces basically three types of products which are solid, liquid and gas. The yield of liquid product can be as high as 75% by weight [2]. The liquid product contains various organic and inorganic compounds like aldehydes, ketones, hydrocarbons, organic acids etc. The liquid product can be separated into various fractions using suitable methods out of which some can serve as fuel while others can be used as important chemicals or as a starting material for the production of many other important products.

Biofuels were considered as the first transportation fuel. The first cars ever built were made to function on biofuels rather than the conventional fuels. The first internal combustion engine to be

patented in the US in 1826 was designed to run on a blend of ethanol and turpentine (derived from pine trees). Henry Ford designed his original 1908 model T to function on ethanol. Rudolph Diesel intended to power his engine with vegetable oil.

The first biodiesel plant in India was setup in the year 2006 at Kakinada, a city of Andhra Pradesh. This plant uses Belgian technology to produce about 30 million gallons of bio diesel per year from *Jatropha* seeds. This fuel is cheaper than the conventional diesel and had been used as a substitute to conventional diesel. All in all, there are biodiesel plants in more than 9 states of India. Indian Railways is the first consumer of biodiesel in the Public Sector. Generally the fuel used by Indian railways is a blend of biodiesel and conventional diesel in various proportions and is efficiently used in the diesel engines of the railway locomotives.

Presently, various researches are going on biodiesel fuel for finding more and more suitable crops to enhance the oil yield. A company named Ecofasa with a group of Spanish developers announced a new biodiesel fuel which was made from trash. Currently a research has been done by the U.S. NREL on biodiesel fuel which involves experimenting with algae which have 50% more natural oil content, so that it can be used as a biodiesel source. A group at the Russian Academy of Sciences in Moscow had used some single-celled algae as biodiesel fuel research. They stated that they had separated large amounts of lipids from these fungi in an economically efficient manner. Some researchers recently have produced biodiesel fuel from oil obtained from used coffee grounds. The estimated cost of producing biodiesel following this method could be not more than about one US dollar per gallon [3].

These days TGA is used frequently for the kinetic study of biomass [4,5]. TGA is generally preferred due to its simplicity and its dependence on fewer observations for the calculation of the kinetics for the complete temperature range [6]. The kinetics of biomass is of great importance in the context of energy recovery. It constitutes the initial step in the process of combustion and gasification. Knowledge of the kinetics for thermal decomposition of lignocellulose (cellulose, hemicellulose and lignin) materials is a necessary requirement for the design and optimization of reactors. Determination of kinetic parameters are useful in determining the thermal behavior of the sample. Therefore, they are important for the design of product features and establishment of

process conditions. The kinetic parameters can be calculated by thermogravimetric analysis (TGA). This technique allows measurement of mass change versus temperature and the results are expressed in the form of curves of weight loss (TGA) and derivative mass loss (DTG).

In this present work, the thermal pyrolysis of simal cotton seed was performed in a semi-batch reactor at different reaction conditions viz. temperature range of 450-700°C and at a constant heating rate of 20°C min⁻¹. The effect of temperature and feed size on product yield was studied and its characterization was done. Also, its kinetic study was done in which we present a comparison between the model-fitting method of Coat and Redfern, the non-isoconversional method of Kissinger and isoconversional method of FWO and KAS.

Chapter 2

(LITERATURE REVIEW)

2. Literature Review

2.1 Biomass

Biomass refers to any organic material derived from plants and animals. Biomass is non-fossilized and bio-degradable organic material originating from plants, animals and micro-organisms. This includes the products, by-products, residues and wastes from agriculture, forestry, industrial and municipal wastes.

The major constituents of biomass are cellulose, hemicellulose and lignin.

2.1.1. Cellulose

It is a complex carbohydrate or polysaccharide consisting of around 3000 or more glucose units. It is the primary constituent of the biomass cell wall. It is represented by the general formula: $(C_6H_{10}O_5)_n$. It is derived from D-glucose units which condense from β (1-4) glycosides linkage. It is crystalline in nature and insoluble in water and most organic solvents. It comprises about 33% of all vegetable matter.

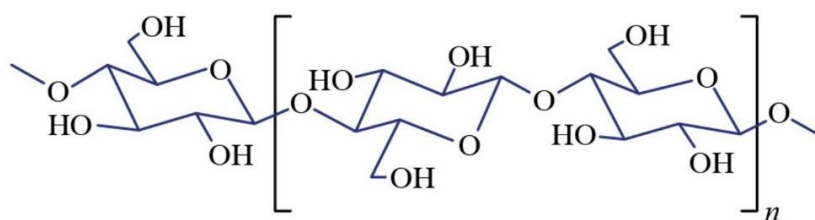


Fig. 2.1 Molecular structure of cellulose

2.1.2 Hemicellulose

It is a polysaccharide present in the plant cell wall along with the cellulose. It is represented by the general formula: $(C_5H_8O_4)_n$. It contains some simple sugar monomers like glucose, xylose, mannose, galactose, ababinose and glucuronic acid. Unlike cellulose, hemicellulose is a branched polymer and consists of shorter chains-500-3000 sugar units as compared to cellulose which has

7000-15000 glucose molecules per polymer. It is soluble in weak alkaline solutions and is easily hydrolyzed by dilute acids and bases. It constitutes around 30-40% of the dry weight of most wood. Due to presence of hemicellulose biomass produces more gases and less tar than cellulose at the time of decomposition.

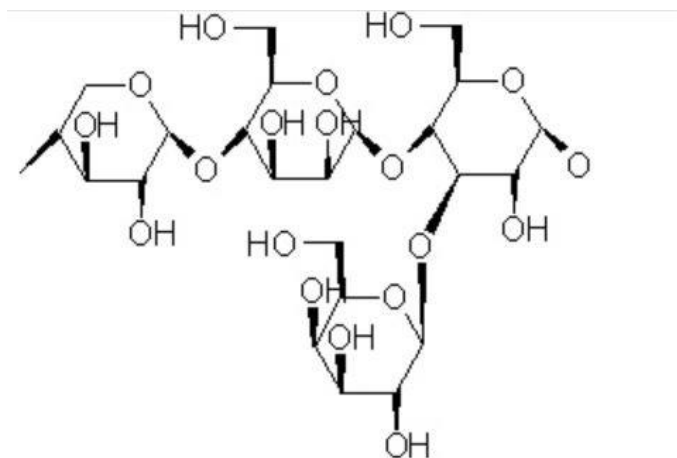


Fig. 2.2 Structure of Hemicellulose

2.1.3. Lignin

Lignin, which is also an important constituent of woody biomass is complex in nature, highly branched polymer of phenyl propane and is a major part of the secondary cell walls of plants. It is primarily a 3-D polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2,5-dimethoxyl phenol. It is one of the most abundant organic polymers on Earth (exceeded only by cellulose). Lignin acts as a binding agent for cellulose fibers holding its adjacent cells together. The monomeric units dominantly present in the polymers are benzene rings. It is highly insoluble, even in sulfuric acid. A typical hardwood contains about 18 to 25%, while softwood contains 25 to 35% by dry weight of lignin.

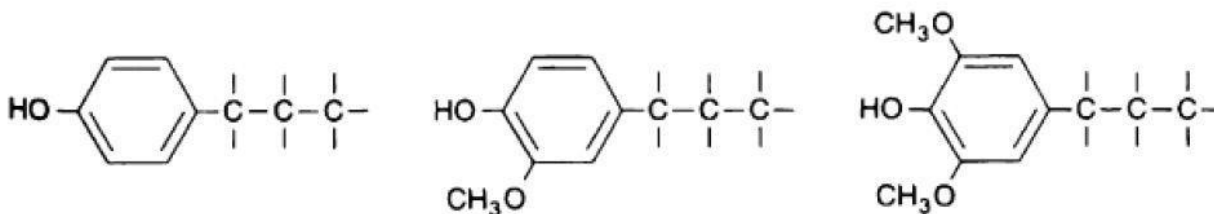


Fig. 2.3 Structure of lignin

2.2 Bio-fuels

The fuels obtained from biomass are called biofuels. In order to consider as a bio-fuel, the fuel must contain 80% renewable materials. Bio-fuel includes solid biomass, liquid fuels and gaseous fuels. Solid biofuel includes wood, saw dust, grass cuttings, domestic refuse, charcoal, agricultural wastes, non-food energy crops and dried manure whereas liquid fuel includes bio-diesel, bio-alcohol, bio-ether, pyrolytic oil and gaseous fuel includes syngas and bio-gas.

2.3 Conversion of biomass into bio-fuels

Biomass can be converted to bio-fuels by three main processes:

1. Physical process
2. Biological process
3. Thermo-chemical process

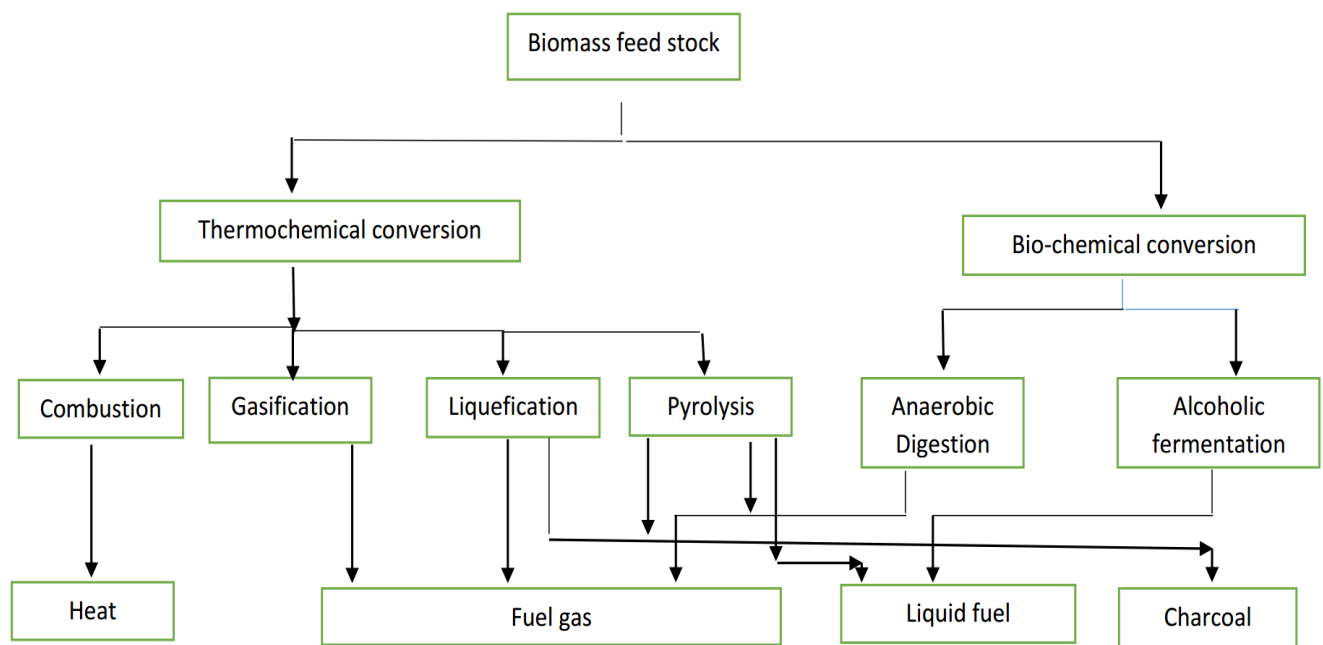


Fig. 2.4 Biomass feedstock conversion by different methods.

2.3.1 Physical process

The physical process of conversion is generally applicable to oil seeds. In the process, oil is extracted from the seeds bearing oil and the extracted oil is then subjected to esterification with alcohol to reduce its viscosity and improve its quality.

2.3.2 Bio-chemical process

This process is mostly used for semi solids or liquid biomass having high percentage of water. It mainly depends on the action of micro-organisms on wet biomass in presence or absence of oxygen.

2.3.3 Thermo-chemical process

In this process, the feedstock is heated in the presence or absence of oxygen or water for a considerable amount of time. The product obtained are fuel gases and bio-oils, which can be used as fuels directly or are blended with other fuels to increase the efficiency or can be treated by various process to produce useful chemicals.

The two main Thermo-chemical process are:

1. Gasification
2. Pyrolysis

2.3.3.1 Gasification

When biomass is heated with only about one-third of the oxygen needed for efficient combustion, it gasifies to a mixture of CO and H₂. The gaseous mixture is called synthesis gas or syngas.

2.3.3.2 Pyrolysis

Pyrolysis is mainly concerned with thermo-chemical process for conversion of biomass. It involves heating the biomass at high temperature in the absence of air which produces gaseous products and later can be condensed to give liquid fuels consisting of bio-oil and oily water (mixture of water and certain hydrocarbons). About 70-80% of gaseous products can be converted to liquid products if the operational conditions are good. This process produces good quantity of liquid fuel

from biomass which is very similar to transportation fuel and can be upgraded to replace transportation fuel. [7]

It also produces some amount of gaseous and solid products which can also be used as a source of energy.

Mostly all the three products i.e. solid, liquid and gaseous products are produced but their composition can vary by the adjustment of the process parameters. With most biomass, low in ash a high yield of liquid is obtained.

2.3.4 Pyrolytic products

As we know, pyrolysis involves breakdown of a large complex molecule into various smaller molecules. Mainly three types of pyrolytic products are obtained:

- **Solid**

The solid product produced during the pyrolysis process is mostly char. It is mainly carbon (around 85%), but it can also contain some oxygen and hydrogen. As compared to fossil fuels, it contains very little inorganic ash.

- **Liquid**

The liquid produced consist mainly tar, bio-oil and water. The bio-oil is dark brown or black viscous liquid that can contain up to 20% of water. Bio-oil is basically a micro-emulsion in which the continuous phase is an aqueous solution of the products of cellulose and hemicellulose decomposition, and small molecules from lignin decomposition. The discontinuous phase is largely composed of pyrolytic lignin macromolecules (Piskorz et al., 1988). Following compound are mainly present in bio-oil:

- Hydroxyaldehydes
- Hydroxyketones
- Sugars and dehydrosugars
- Carboxylic acids
- Phenolic compounds

- **Gas**

Primary decomposition of biomass produces both condensable gases and non-condensable gases. The condensable gases, which contain heavier molecules, condense upon cooling and are collected as pyrolytic liquid product. The non-condensable gas mixture contains lower molecular-weight gases like carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4). These gases do not condense on cooling. At high temperature, due to cracking of the vapor, some additional non-condensable gases are produced which are called secondary gases. So the final non-condensable gas product contains both primary and secondary gases.

2.3.5 Features of pyrolysis process required to obtain liquid product

1. To improve the heat transfer between the feed particles, the typical feed size of biomass should be less than 3mm.
2. The pyrolysis temperature should be around 500 °C so that the liquid yield obtained is maximum.
3. To minimize the secondary reactions the vapor residence time should be less than 2 sec.
4. The char produced during pyrolysis is removed as soon as it is formed to minimize cracking of vapors.
5. The vapors produced during pyrolysis are rapidly cooled to give the liquid product [8,9].

Liquid product which is bio-oil, is obtained in yields of up to 75 wt. % on a dry-feed basis, together with by-product char and gas which is used within the process to provide heat requirements so that there are no waste streams other than flue gas and ash. Liquid product depends on hot vapor residence time, biomass ash content, biomass type, temperature, and hot vapor residence time and char separation [10].

Prior to pyrolysis, the material is dried to less than 10% water in order to minimize the water content in the product liquid oil, the feed is grinded to give sufficiently small particles to ensure rapid, fast and efficient separation of solids (char), and rapid quenching and collection of the liquid products.

Pyrolysis is an advantageous process because it can convert biomass directly into liquid, solid and gaseous products by thermal decomposition of biomass in the absence of oxygen. [11]

Pyrolysis is of two types:

2.3.3.2.1 Fast pyrolysis

In fast pyrolysis process the feedstock is rapidly heated in the absence of oxygen at high temperature. During decomposition biomass generates vapors, aerosols and charcoal like char. After cooling and condensation of the vapors and aerosols a dark brown mobile liquid is formed that has a heating value of half of that of conventional fuels [12].

Fast pyrolysis process produces 60-75 wt. % liquid bio-oil, 15-25 wt. % of solid char and 10-20 wt. % of non-condensable gases, depending on feedstock used. The bio-oil and solid char produced can be used as a fuel and the gas can be recycled back into the process.

Fast pyrolysis of rapeseed was studied by Kockar et al [13] and investigated effect of temperature, heating rate, particle size and sweep gas flow on the product yield and concluded that the yield of char decreases to 14.5% from 27% with increase in temperature and maximum 73% yield of oil at a temperature of 550-600°C particle size of +0.6-1.25 mm and sweep gas flow rate of 100 cm³/min.

2.3.3.2.2 Slow pyrolysis

When pyrolysis is carried out at slow heating rate (3-7 K/min), it is known as slow pyrolysis. Various literature shows that in slow pyrolysis, the yield of oil is less and yield of char is more [14, 15].

2.3.6 Application of pyrolytic products

The application of the common products obtained from pyrolysis of biomass is given below:

2.3.6.1 Application of pyrolytic oil

The bio-oil obtained from pyrolysis can have the following industrial applications:

- Can be used as a fuel
- power generation
- For extraction of chemicals and resins
- As a binding agents
- For blending with diesel
- Can be used in making adhesives

2.3.6.2 Application of pyrolytic gases

Pyrolysis gas consists light hydrocarbons like carbon dioxide, carbon monoxide, methane, ethane, ethylene etc. which can be used as fuel for combustion.

2.3.6.3 Application of pyrolytic char

The char obtained has following applications:

- Solid fuel in boilers after briquetting
- Used as an adsorbent because of its porous structure and high surface area,
- For gasification process to obtain hydrogen rich gas.
- Can be used for carbon sequestration to decreases environmental CO₂.

Chapter 3

(MATERIALS AND METHODS)

3. Materials and methods

3.1 Raw material

Simal cotton seed (*Bombax malabarica*) has been used as the raw material for the pyrolysis experiments. It belongs to malvaceae family. It has different names in different part of India, commonly known as simal, simbal, pagun, semur etc. It is found in almost every part of India, Sri Lanka, Burma and Malaysia only except areas with dry and arid climate. Before carrying out pyrolysis experiments, the seeds were grinded to fine powder and then dried in an oven at about 105°C to remove all the free moisture. Simal cotton seed is shown in fig 3.1 and its powder is shown in fig 3.2.



Fig. 3.1 Simal cotton seed



Fig 3.2 Simal cotton seed powder

3.2 Characterization of raw material

Biomass characterization is essential to predict its behavior as a fuel. Proximate and ultimate analysis are the important methods used for its characterization.

3.2.1 Proximate analysis

Proximate analysis estimates the % of moisture, volatile matter, ash and fixed carbon content in a sample. The procedure to estimate each of these quantities is as follows:

I. Determination of moisture content

Known amount of air dried sample was taken in a crucible and kept in an electrically heated oven at a temperature of 105°C for about one and a half hour. After that the sample was taken out and cooled in a desiccator. The percentage loss of weight gave the percentage of moisture present in the sample.

Percentage of moisture content = $\text{loss in weight} \times 100 / \text{wt. of sample taken}$

II. Determination of volatile matter

1 gm of sample was then taken in a cylindrical crucible and kept in an electrically heated furnace with the lid at a temperature of 925°C for about seven minutes and then cooled in a desiccator. The percentage weight loss gave the volatile matter content.

Percentage of volatile matter = $\text{loss due to removal of volatile matter} \times 100 / \text{wt. of sample taken}$

III. Determination of ash content

1 gm of sample was taken in a crucible and kept in the furnace at a temperature of around 750°C for about one and half hour. The percentage of weight loss gave the ash content.

Percentage of ash = $\text{weight of ash left} \times 100 / \text{wt. of sample taken}$

IV. Determination of fixed carbon

Percentage of fixed carbon = $100 - \% \text{ of (moisture + volatile + ash) content}$

3.2.2 Ultimate Analysis

Ultimate analysis is used to determine the elemental composition of the sample which includes determination of carbon, hydrogen, nitrogen, sulfur, oxygen contents of the material. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of these compositions is subtracted from 100, it gives oxygen percentage composition.

3.3 Characterization of pyrolytic oil

The pyrolytic oils obtained were characterized for their physical and chemical properties. The physical properties such as viscosity, density, calorific value, pH, flash point, fire point, pour point of the pyrolytic oil were determined using standard methods and mentioned in the result and discussion part.

The calorific value was measured using Parr 6100 digital bomb calorimeter and flash point and pour point by flash point apparatus and pour point apparatus.

3.3.1 FTIR analysis of pyrolytic oil

Fourier Transform Infrared spectroscopy (FTIR) is an important technique that detects the presence of various characteristic functional groups in oil. Due to interaction of an infrared light with oil the chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range in the presence of the rest of molecules. The above principle was used to identify the functional groups present in the pyrolytic oil. The FTIR spectra were collected generally in the range of $400\text{--}4000\text{ cm}^{-1}$ region with 8 cm^{-1} resolution. The FTIR analysis was carried out using Perkin Elmer Infra-red Spectrometer. The FTIR instrument is shown in fig. 3.3

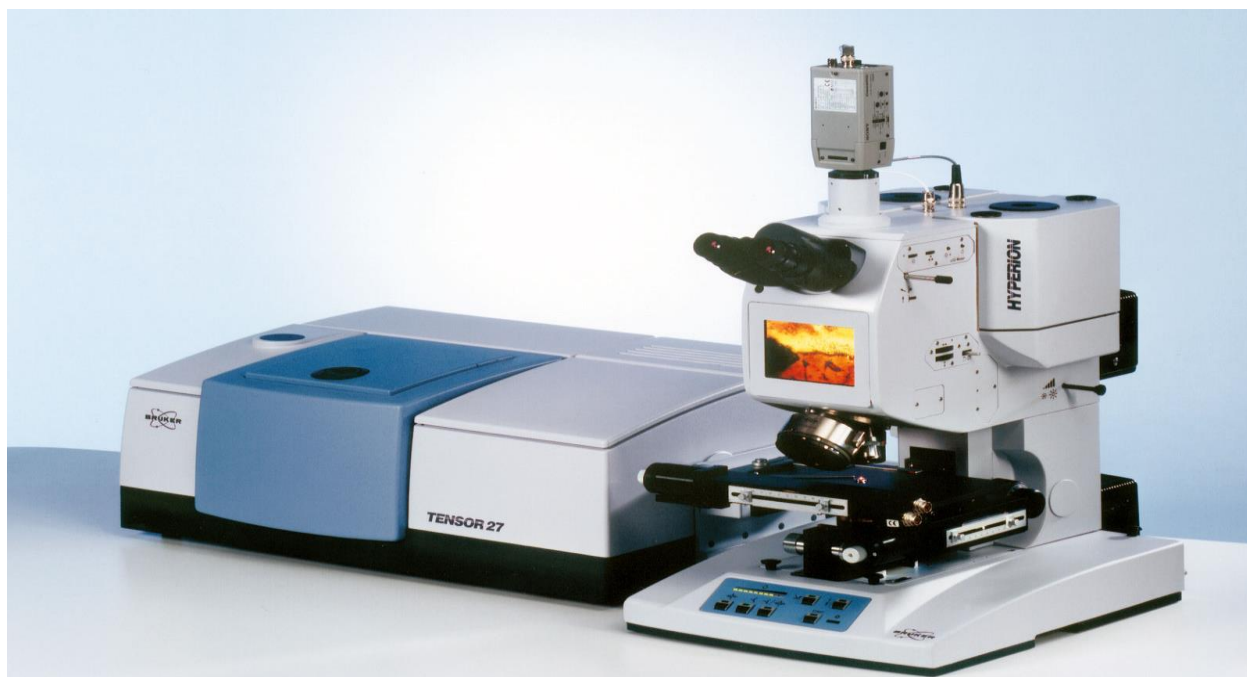


Fig. 3.3 FTIR instrument

3.3.2 GC-MS analysis of pyrolytic oil

The pyrolytic oil was characterized by using GC-MS QP 2010[SHIMADZU] which is shown in fig 3.4. Gas chromatography- Mass Spectroscopy is an analytical method that combines the feature of gas-liquid chromatography and mass spectroscopy to identify different substances within a test sample. For GC-MS the sample was first dissolved in n-Hexane in the ratio of 1:20 and a clear solution was obtained. The solution was then filtered using 2 micron membrane filter



Fig.3.4 GC-MS QP 2010[SHIMADZU] instrument

3.4 Characterization of pyrolytic char

The pyrolytic char was characterized according to their calorific value, pore structure, and elemental analysis. The calorific value was measured using bomb calorimeter and SEM/EDX for pore structure and elemental analysis.

3.5 Thermogravimetric Analysis (TGA)

3.5.1 Methods for studying solid state kinetics

There are various methods which are used to study solid-state kinetics. These methods are grouped in two categories: experimental methods and computational method[16].

3.5.1.1 Experimental method

There are two methods for the study of solid state kinetic data which are isothermal method and non-isothermal method.

3.5.1.1.1 Isothermal method: In isothermal method the sample is heated at several constant temperatures. Change in weight is obtained for different time at each constant temperature. This method is based on isothermal rate equation.

3.5.1.1.2 Non isothermal method: In non-isothermal method the sample is heated at constant heating rate (β). Change in weight is obtained at different temperatures for several constant heating rates and this method is based on the non-isothermal rate equation.

$$\beta = \frac{dT}{dt}$$

We know that the rate expression is represented as:

$$\frac{d\alpha}{dt} = A e^{-\frac{E}{RT}}$$

The LHS of the above equation can be written as:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} \quad \left(\frac{dT}{dt} = \beta \right)$$

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \frac{1}{\beta}$$

Where $\frac{d\alpha}{dT}$ is the non-isothermal rate of reaction is, $\frac{d\alpha}{dt}$ is the isothermal rate of reaction and β is the rate of reaction.

Now the non-isothermal reaction rate can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha)$$

Putting $f(\alpha) = (1-\alpha)^n$ we get,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} (1-\alpha)^n$$

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} e^{-\frac{E}{RT}} dT$$

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \int_0^T \frac{A}{\beta} e^{-\frac{E}{RT}} dT$$

It is not possible to integrate directly the R.H.S. of this equation as it has no analytical form while the L.H.S. of the equation can be integrated for different values of n. The integral on the R.H.S. is known as the temperature integral.

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-\frac{E}{RT}} dT$$

$$\text{Take, } I = \int_0^T e^{-\frac{E}{RT}} dT$$

$$\text{Take } x = \frac{E}{RT}$$

$$dx = -\frac{E}{RT^2} dT \quad \text{Hence, } dT = -\frac{RT^2}{E} dx$$

Now evaluating the new limits,

$$\text{When } T = 0 \quad x = \infty$$

$$\text{When } T = T \quad x = \frac{E}{RT} \text{ i.e. } x$$

Hence, putting the value of dT and applying new limits the integral becomes,

$$I = -\frac{E}{R} \int_\infty^x \frac{e^{-x}}{x^2} dx$$

$$= \frac{E}{R} \int_x^\infty \frac{e^{-x}}{x^2} dx$$

Therefore, $g(\alpha)$ becomes,

$$g(\alpha) = \frac{AE}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2} dx$$

If, $\int_x^\infty \frac{e^{-x}}{x^2} dx = p(x)$

Then, $g(\alpha) = \frac{AE}{\beta R} p(x)$

Here, $p(x)$ is the exponential integral. Following approaches are used to evaluate $p(x)$.

1. Value of $p(x)$ is calculated numerically.
2. $p(x)$ is converted to an approximate form that can be integrated.
3. $p(x)$ is finally approximated by a series expansion.

3.5.1.2 Calculation methods

There are two group of methods which can be used to analyze either isothermal or non-isothermal solid state kinetic data:

- 1) Model fitting method
- 2) Model-free method

3.5.1.2.1 Model fitting methods

In this method different models are fitted to the data and the model which gives the best statistical fit is chosen to calculate the kinetic parameters i.e. the activation energy and the pre-exponential factor.

Advantage: In this method only a single TGA measurement is required for determination of kinetic parameters.

Disadvantage: This method involves a single TGA measurement which is not sufficient enough to determine the reaction kinetics.

3.5.1.2.2 Model free method (isoconversional method)

Model free method determines the dependency of the activation energy on the extent of conversion and permits reliable physical conclusion to be drawn. Several kinetic curves are required in this method to perform the analysis.

Advantage: It is much simpler and it avoids the errors connected with the choice of kinetic model.

Disadvantage: It needs at least three TGA measurements which makes it more time consuming method.

All isoconversional methods are model-free but all model free methods are not isoconversional e.g. - Kissinger method because in this method the activation energy doesn't depends on conversion. It remains constant throughout the process.

3.5.2 Integral Coat and Redfern Method

As we know every Kinetic model obeys the Arrhenius equation,

$$k(T) = Ae^{-\frac{E}{RT}}$$

And the rate of the reaction is given by:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}(1 - \alpha)^n$$

Here, A is the frequency or pre-exponential factor, E is the activation energy of the reaction, R is the universal gas constant, T is the absolute temperature, n is the order of reaction, t is the time, and α is the fraction of reactant decomposed at time t.

We know that the constant heating rate $\beta = \frac{dT}{dt}$

Hence,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} (1 - \alpha)^n$$

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} e^{-\frac{E}{RT}} dT$$

Integrating both sides, we get:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_0^T e^{-\frac{E}{RT}} dT$$

Since, $\int_0^T e^{-\frac{E}{RT}} dT$ does not have any exact integral value, so $e^{-\frac{E}{RT}}$ can be expressed as an asymptotic series and its integration after ignoring the higher order terms gives:

$$1 - \frac{(1-\alpha)^n}{(1-n)} = \frac{ART^2}{\beta E} \left(1 - \frac{2RT}{E}\right) e^{-\frac{E}{RT}}$$

Taking logarithm of both the sides, we get:

$$\ln \left[1 - \frac{(1-\alpha)^n}{(1-n)T^2}\right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{For } n \neq 1$$

If we assume that $\frac{2RT}{E} \ll 1$ then we get:

$$\ln \left[1 - \frac{(1-\alpha)^n}{(1-n)T^2}\right] = \ln \left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad \text{For } n \neq 1 \quad \rightarrow (1)$$

For further simplification we can assume the order of the reaction to be unity.

Hence the above equation becomes:

$$\ln \left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln \left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad \text{For } n = 1 \quad \rightarrow (2)$$

Plotting a graph between L.H.S. of the equation for $n=1$ or $n \neq 1$ versus $1/T$ we can calculate the Activation Energy (E) and the Frequency factor (A) from the slope and the intercept of the graph.

3.5.3 Kissinger Method

In this method the energy of activation (E) is evaluated from a plot of $\ln\left(\frac{\beta}{T_m^2}\right)$ versus $\frac{1000}{T_m}$ for a series of experiments at different heating rates (β). T_m is the peak temperature can be obtained from the DTG curve. It is the temperature at which maximum weight loss take place.

The Kissinger[6] equation is shown below:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m}$$

Here $-\frac{E}{R}$ is the slope of the plot from which activation energy can be calculated.

This equation can be derived from the general rate equation:

$$\frac{d\alpha}{dT} = Ae^{-\frac{E}{RT}} f(\alpha) \quad \rightarrow (3)$$

Now, if the second derivative for the above reaction is zero then the reaction rate is maximum.

Differentiating the general rate equation both sides, we get:

$$\frac{d}{dt}\left[\frac{d\alpha}{dT}\right] = Ae^{-\frac{E}{RT}} \frac{d}{dt}[f(\alpha)] + Af(\alpha) \frac{d}{dt}\left[e^{-\frac{E}{RT}}\right] \quad \rightarrow (4)$$

β is the constant heating rate $\frac{dT}{dt}$

$$\text{And } \frac{d}{dt}\left[e^{-\frac{E}{RT}}\right] = \frac{E\beta}{RT^2} e^{-\frac{E}{RT}}$$

At the maximum of the DTG curve $T = T_m$ and $\frac{d}{dt}\left[\frac{d\alpha}{dT}\right] = 0$

Therefore equation (2) becomes:

$$0 = \frac{d}{dt}[f(\alpha)] + f(\alpha) \frac{E\beta}{RT_m^2}$$

Now we know that, $f'(\alpha) = \frac{d}{d\alpha}[f(\alpha)]$

$$\text{Then } \frac{d}{dt}[f(\alpha)] = \frac{d}{d\alpha}[f(\alpha)] \times \frac{d\alpha}{dt}$$

$$= f'(\alpha) \frac{d\alpha}{dt}$$

Putting this value in above equation, we get:

$$Ae^{-\frac{E}{RT_m}} f'(\alpha) + \frac{E\beta}{RT_m^2}$$

Solving for $\frac{\beta}{T_m^2}$ and taking the natural logarithm we get

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) + \ln[-f'(\alpha)] - \frac{E}{RT_m}$$

If reaction is assumed to be of first order (n=1) and $f(\alpha) = (1-\alpha)$, $f'(\alpha) = -1$

$$\ln[-f'(\alpha)] = 0$$

Thus the above equation becomes

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \rightarrow (5)$$

Which is the Kissinger equation.

3.5.4 Flynn-Wall-Ozawa method

The Flynn-Wall-Ozawa method[4,5] is a model-free method in which temperature is measured for different heating rates(β) at a constant value of conversion(α) from a plot of conversion versus temperature and a graph between $\ln(\beta)$ and $1/T$ is plotted. Activation energy can be obtained from the slope of the plot.

We know that, the non-isothermal rate law is given as:

$$g(\alpha) = \frac{AE}{\beta R} p(x)$$

Taking Logarithm on both sides, we get:

$$\log g(\alpha) = \log \frac{AE}{\beta R} + \log p(x) \dots (6)$$

From Doyle's Approximation which shows that for a short range of x , $\log p(x)$ and x is linear.

$$\log p(x) \approx -A - Bx$$

Where $28 < x < 50$

By interpolation, $A=5.3305$ and $B=1.052$

$$\therefore \log p(x) \approx -5.3305 - 1.052x$$

Substituting Doyle's Approximation in equation (4) we get:

$$\log g(\alpha) = \log \frac{AE}{\beta R} - 5.3305 - 1.052x$$

Putting E/RT in place of x , we get:

$$\log g(\alpha) = \log \frac{AE}{\beta R} - 5.3305 - 1.052 \frac{E}{RT}$$

Now, rearranging the above equation we get:

$$\log \beta = \log \frac{AE}{g(\alpha)R} - 5.3305 - 1.052 \frac{E}{RT} \rightarrow (7)$$

Above equation is the desired equation. Plotting $\log(\beta)$ vs $1/T$ for different values of conversion we can calculate activation energy (E) from the slope, irrespective of the model.

3.5.5 Kissinger-Akahira-Sunose Method

KAS method [1,13] uses the following expression

$$\ln \left(\frac{\beta_i}{T_{\alpha,i}^2} \right) = \ln \left(\frac{A_\alpha R}{E_\alpha} \right) - \ln g(\alpha) - \frac{E_\alpha}{RT_{\alpha,i}}$$

This equation is derived as shown below

The overall rate of reaction is given by

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad \dots (8)$$

Where $\frac{d\alpha}{dt}$ is the reaction rate, α is the conversion degree, $k(T)$ is the rate constant, t is the time, T is the temperature, and $f(\alpha)$ is the reaction model.

The rate constant $k(T)$ is described by the Arrhenius Law

$$k(T) = Ae^{-\frac{E}{RT}} \quad \dots (9)$$

Where E is the activation energy, A is the pre-exponential factor or frequency factor and R is the gas constant.

Now, we know that $\beta = \frac{dT}{dt}$, where β is the heating rate.

Therefore we can write equation (8) as following:

$$\frac{d\alpha}{dT} = \frac{k(T)f(\alpha)}{\beta}$$

Or

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha)$$

Which is the differential non-isothermal rate law.

Integrating both sides we get,

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-\frac{E}{RT}} dT$$

This equation does not have any analytical solution. So it can be written as:

$$g(\alpha) = \frac{AE}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2} dx$$

$$\text{Put } \int_x^\infty \frac{e^{-x}}{x^2} dx = p(x)$$

$$\therefore g(\alpha) = \frac{AE}{\beta R} p(x) \quad \dots\dots (10)$$

From the approximation used by Murray and White,

$$p(x) \cong \frac{e^{-x}}{x^2}$$

Which is valid for $20 < x < 50$

Where $x = E/RT$

Putting value of $p(x)$ and x in equation (10), we get:

$$g(\alpha) = \frac{AE}{\beta R} \frac{e^{-\frac{E}{RT}}}{\left(\frac{E}{RT}\right)^2}$$

Rearranging, we get:

$$\frac{\beta}{T^2} = \frac{AR}{Eg(\alpha)} e^{-\frac{E}{RT}}$$

Taking logarithm on both sides, we get:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) - \ln g(\alpha) - \frac{E}{RT}$$

For a constant conversion value we can write the above equation as:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \ln\left(\frac{A_{\alpha}R}{E_{\alpha}}\right) - \ln g(\alpha) - \frac{E_{\alpha}}{RT_{\alpha,i}} \quad \rightarrow (11)$$

The Activation Energy can be evaluated from the above equation by plotting the L.H.S. of the equation against $\frac{1}{T_{\alpha,i}}$ at constant conversion for the ith heating rate.

Chapter 4

(EXPERIMENTAL SETUP)

4. Experimental Setup

4.1 Experimental setup and procedure

The experiments were conducted in a reactor-furnace system shown in fig 4.1 in which the furnace temperature was maintained constant using a PID controller. The outlet of reactor was attached to a series of condenser to condense the vapors coming out of it and was collected in a measuring cylinder at the outlet of the condenser. Finely grinded and sieved simal cotton seed sample was filled in a reactor of 208.55 ml capacity and the reactor was kept in the furnace for heating at constant temperature. The start of the reaction is indicated by vapors coming out of reactor through the reactor outlet. These vapors get condensed in a condenser. Water is used as cooling medium in the condenser and circulated via a pump. The condensed vapors are collected in a container as the liquid product whereas there is some amount of non-condensable gases which are simply left out. The char produced can be obtained from the reactor after it cools down. The liquid product collected contains two phases i.e. the bio-oil phase and the aqueous phase or oily water. The oily water is basically water with some dissolved hydrocarbons. Oily-water and bio-oil is further separated by difference in their density in a separating funnel. The image of our experimental setup is shown in fig 4.2.

4.1 Reactor Specifications

A semi batch reactor made of stainless steel was used for the pyrolysis process. The height of the reactor was 15.5 cm and the internal and external diameter were 4.16 cm and 6.20 cm. The capacity of the reactor was 208.55 cm³.

4.2 Sample pyrolysis run

After finding the temperature range for maximum decomposition of the biomass from the TGA curve, sample pyrolysis runs were done with 30 gm of seed in that range at intervals of 50 °C to determine the optimum temperature i.e. the temperature at which maximum yield of liquid product is obtained. Various data like weight of the liquid product, weight of the solid product were noted down and the corresponding weight percentages were calculated. Variation in the liquid yield, char yield and gas (volatiles) yield with temperature were studied.

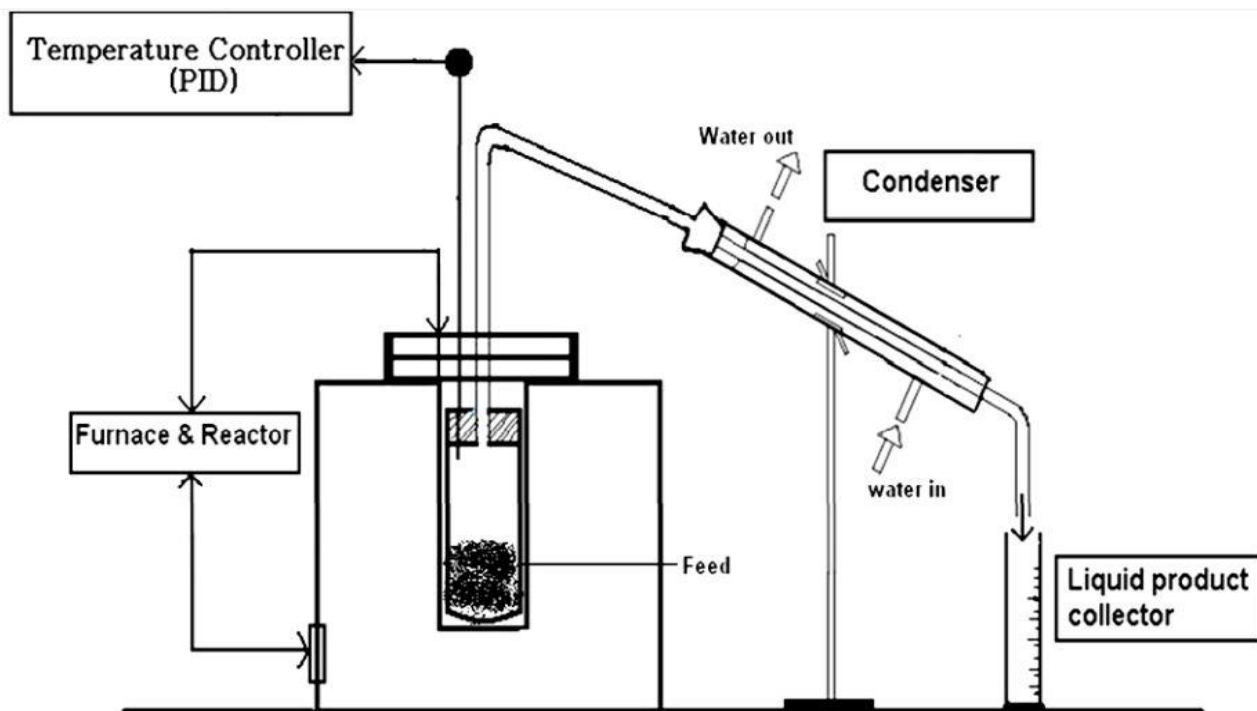


Fig. 4.1 Reactor-furnace arrangement



Fig 4.2 Experimental setup

Chapter 5

(RESULTS AND DISCUSSION)

5. Result and Discussion

5.1 Characterization of Raw material

5.1.1 Proximate Analysis

Table 5.1 shows the result for proximate analysis of simal cotton seed.

Table 5.1

Proximate Analysis of simal cotton seed

Proximate Analysis of simal cotton seed	
Moisture (%)	8.05
Volatile matter (%)	81
Ash (%)	5
Fixed carbon (%)	5.95

Proximate analysis is one of the most efficient method of determining the fuel type and quality. The conversion efficiency of the pyrolytic oil and its heating value are greatly influenced by the moisture content of the biomass. Biomass with high moisture content has a tendency to decompose which results in energy loss during its storage. Here, moisture content is 8.05% which is quite low and thus more favorable. Volatile matter contains mainly combustible gases and light hydrocarbons which can be condensed into liquid. Here, the volatile matter is 81% due to which it gets devolatized more readily than any solid fuel. Fewer ash content and fix carbon percentage obtained here is favorable for producing liquid oil.

5.1.2 Ultimate Analysis

Table 5.2 shows the result for proximate analysis of simal cotton seed.

Table 5.2

Ultimate Analysis of simal cotton seed

Ultimate Analysis of simal cotton seed	
% C	49.84
% H	6.66
% N	7.90
% S	0.20
% O	35.40
H/C molar ratio	1.60
Empirical formula	$\text{CH}_{1.60}\text{N}_{0.14}\text{S}_{0.002}\text{O}_{0.53}$

The ultimate analysis shows that our biomass contains high percentage of carbon followed by oxygen, hydrogen, nitrogen and traces of Sulphur.

5.2 Variation of product yield with temperature of pyrolysis

Table 5.3 shows the variation in yield of various liquid, solid and gaseous product with the variation of pyrolysis temperature. It can be seen from the table that with the increase in pyrolysis temperature, yield of liquid product increases until it reaches a maximum value. For simal cotton seed, this maximum is reached at a temperature of 600°C when the yield is about 58.06% by weight. Beyond this temperature increase in temperature causes decrease in liquid yield. Similar but opposite trend is observed for the char yield. The temperature at which yield of liquid product is maximum, yield of char is minimum.

Table 5.3

Variation of product yield with temperature

Temp (°C)	Liquid wt. (gm.)		Char wt. (gm.)	Wt.% of liquid	Wt. % of char	Wt. % of volatiles
	Bio-oil phase	Aqueous phase				
450	10.41	3.10	9.40	45.03	31.33	23.64
500	12.05	3.78	7.41	52.76	24.70	22.54
550	12.98	4.23	8.10	57.36	27.00	15.64
600	13.15	4.27	7.15	58.06	23.83	18.11
650	13.02	4.07	7.19	56.96	23.96	19.08
700	13.08	3.86	7.24	56.46	24.13	19.41

=

Figure 5.1 gives a graphical representation of the phenomenon mentioned above. The yield of volatile product was determined by method of difference and was not directly measured.

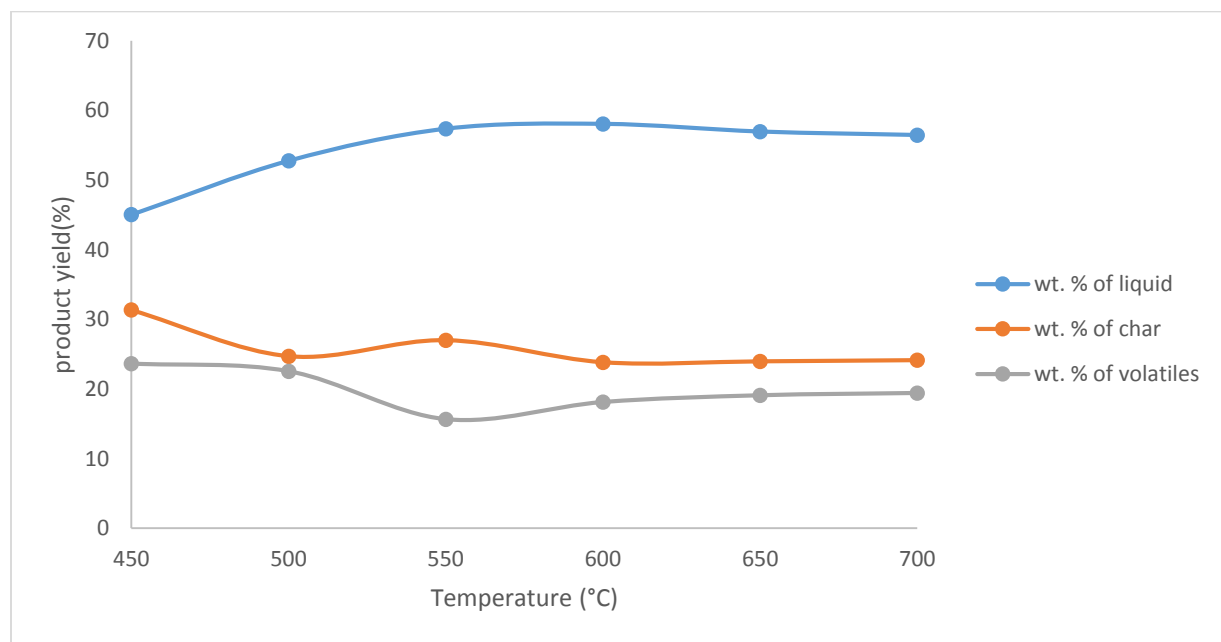


Fig5.1 Variation of product yield with temperature

5.3 Variation of product yield with feed size

Table 5.4 shows the variation in yield of various liquid, solid and gaseous product with the variation of feed size. We can see that the as the feed size decreases yield of pyrolytic oil also increases and yield of pyrolytic char decreases. Beside this the weight % of non-condensable gases also decreases. This variation is observed because of the fact that small feed size provides large surface area for reaction. Heat transfer between the particles is more. So the devolatilization process occurs more readily due to which more condensable vapors are produced which can be condensed to obtain liquid product. Hence, the liquid yield increases with decreasing particle size.

Table 5.4

Variation of product yield with feed size

Feed size (microns)	Liquid wt. (gm.)		Char wt. (gm.)	Wt.% of liquid	Wt. % of char	Wt. % of volatiles
	Bio-oil phase	Aqueous phase				
850	5.84	15.16	18.96	35.00	31.60	33.40
710	19.6	6.96	16.73	44.26	27.88	27.86
600	22.96	6.16	15.94	48.53	26.56	24.91
500	26.30	4.27	14.30	50.95	23.83	25.22

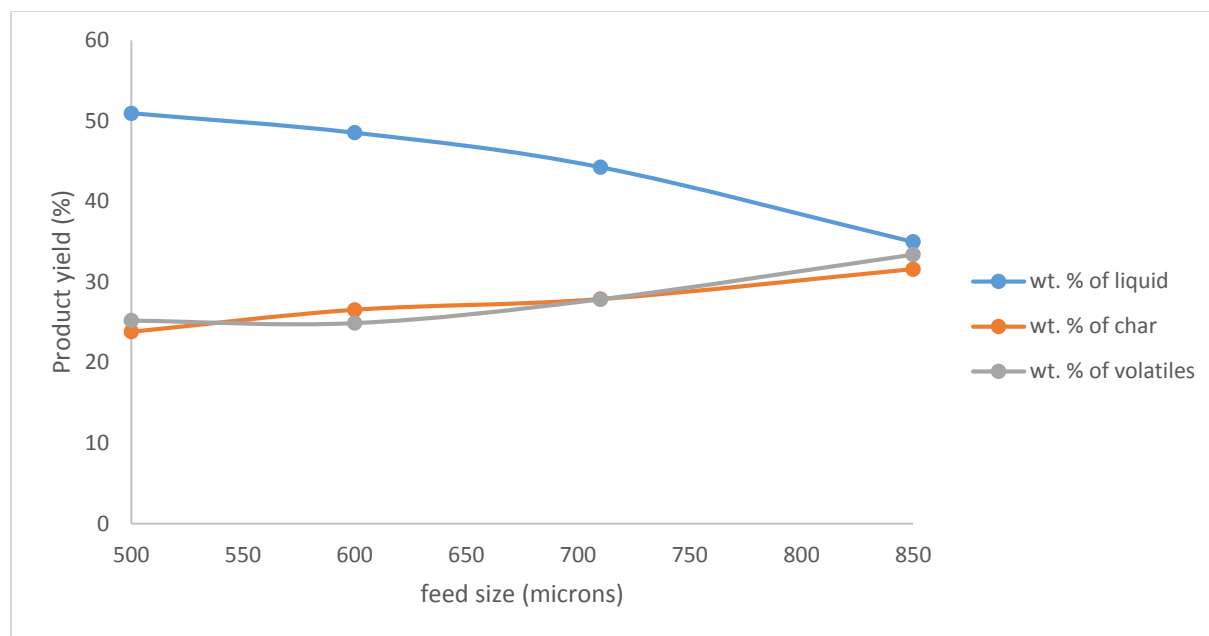


Fig5.2 Variation of product yield with feed size

5.4 Thermogravimetric Analysis

The weight loss curve (TG) for the simal cotton seed (*Bombax malabarica*) is shown in fig. 5.3. It shows the mass loss with increasing temperature at four different heating rates of 5, 15, 25, 30 °C/min. From the plot we can see that there was a slight decrease in weight between the ambient temperature and a temperature of about 500 K. This result was observed because initially the weight loss was due to removal of physically absorbed water or other light volatiles. After 500K, a major change in the slope of the TG curve was observed. This change depicts the start of the devolatilization process due to thermal decomposition of primary hemicellulose and cellulose which proceeds rapidly with increasing temperature till a temperature of around 700 K was achieved. After that the weight loss decreases slowly up to a temperature of 900 K. This region corresponds to the degradation of lignin at higher temperatures. We can see that the solid residue left after decomposition is around 25% for a low heating rate of 5°C/min and it decreases as the heating rate increases. It is around 6% for a heating rate of 25°C/min.

TGA curve was not sufficient enough to interpret the weight loss of the sample. Hence a derivative thermogravimetric (DTG) curve along with the TGA curve was used to determine the apparent weight loss [17].

Differential mass loss (DTG) thermograms of thermal decomposition of simal cotton seed (*Bombax malabarica*) at different heating rates of 5, 15, 25, 30 °C/min under nitrogen atmosphere is shown in fig.5.4.

Three different regions were observed in the plot that corresponds to water removal, active and passive pyrolysis. The first region from 310 K to 450 K corresponds to the removal of moisture and the absorbed water in the seeds. In the second region which corresponds to active pyrolysis, main pyrolysis process was observed to occur in the temperature range of around 450 K to 710 K for a low heating rate of 5°C/min and around 450 K to 730 K for a heating rate of 15°C/min and around 450 K to 750 K for high heating rates of 25 and 30°C/min. Three distinct peaks were observed in this region which was related to the decomposition of hemicellulose, cellulose and lignin[18]. Earlier study on biomass pyrolysis reported that hemicellulose degradation is observed to take place at a temperature lower than 623K, cellulose degradation in a temperature range of 523-773K and lignin decomposition take place at a temperature above 673K[19]. The region after 750 K was the region of passive pyrolysis. Lignin was decomposed in both the active and passive pyrolysis region. With the increase in heating rate, DTG curve shifts towards higher temperature side and the value of T_m which is obtained at the point of maximum conversion also increases.

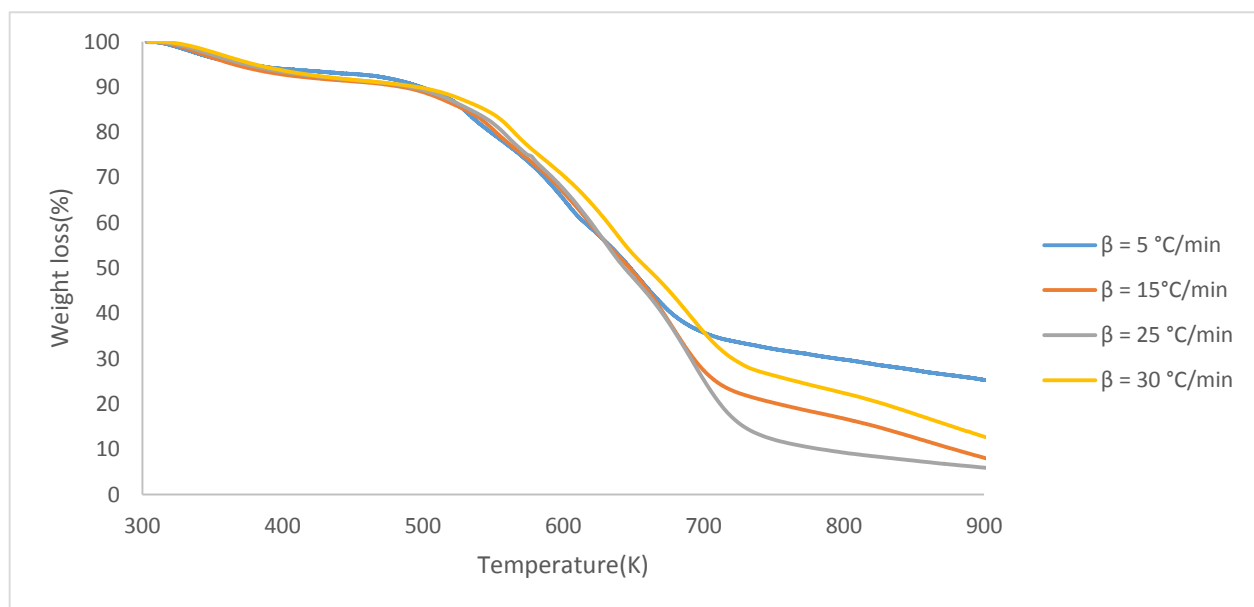


Fig.5.3 TG Weight loss curve of simal cotton seed in nitrogen atmosphere at four different heating rate

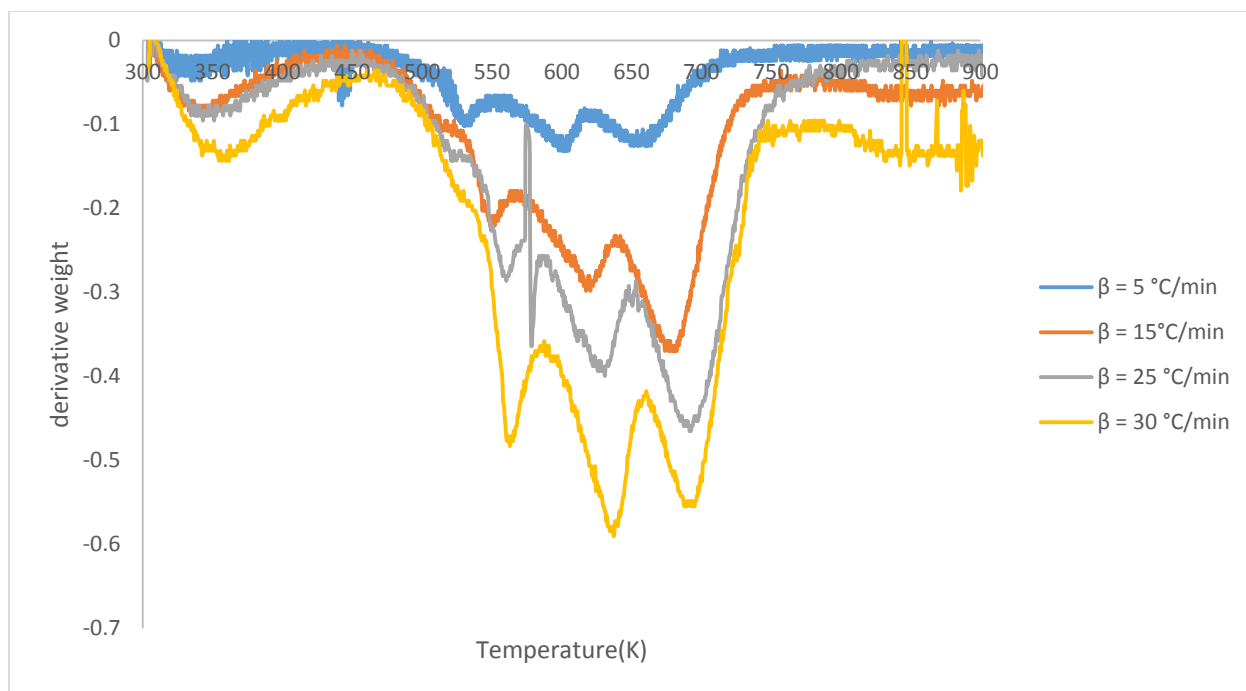


Fig.5.4 DTG curve of simal cotton seed (*Bombax malabarica*) in nitrogen atmosphere at four different heating rate.

5.5 Kinetic Study

The results obtained from thermogravimetric analysis is used to obtain kinetic parameters using different model fitting and model free methods. The kinetic parameters i.e. the activation energy (E) and the pre-exponential factor or frequency factor(A) is calculated by the Coat and Redfern method, Kissinger method, FWO and KAS method.

5.5.1 Coat and Redfern method

In the Coat and Redfern method the Activation energy (E) and the pre-exponential factor (A) is calculated by equation (2).The plot of $\ln \left[-\frac{\ln(1-\alpha)}{T^2} \right]$ vs $\frac{1}{T}$ is shown in fig. 5.5. The regression equation and the square of the co-relation coefficient is also presented. The Activation energy and the pre-exponential factor calculated respectively from the slope and intercept of the regression equation is tabulated in table 5.4

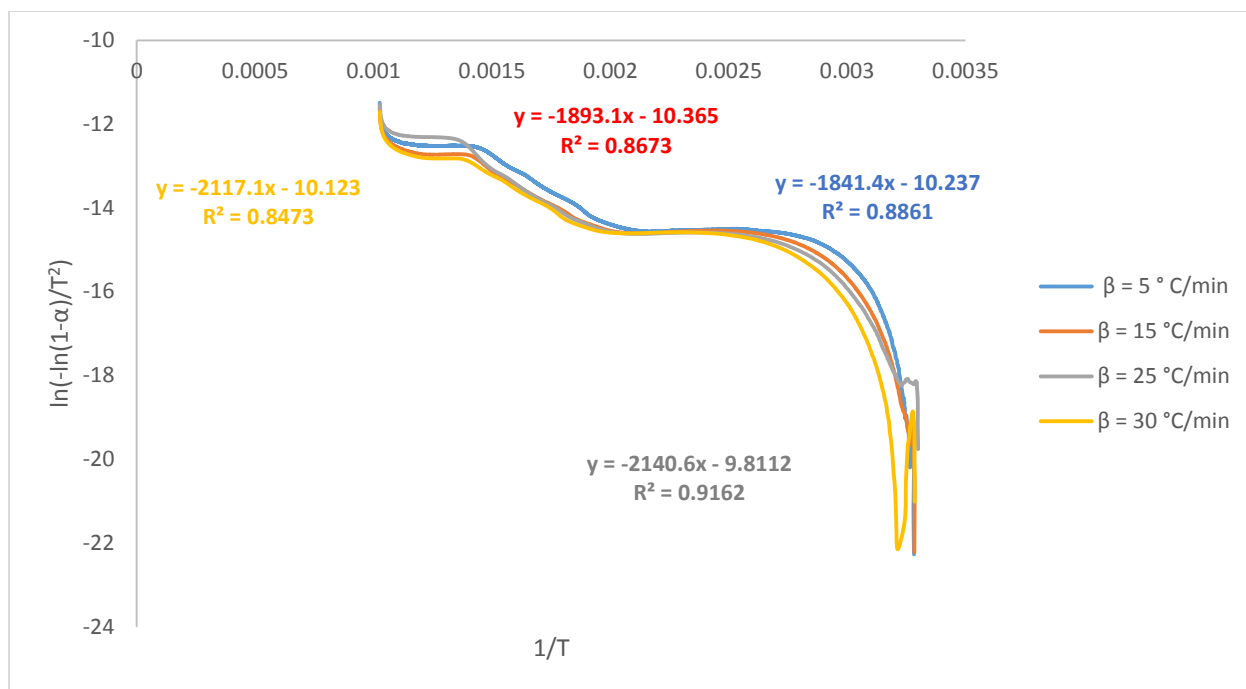


Fig.5.5 Coat and Redfern plot for four different heating rates

Table 5.5

Kinetic parameters for Coat and Redfern method

Coat and Redfern Method			
Heating rate (β) ($^\circ\text{C/min}$)	Activation Energy (A) (KJ/mol)	Pre-exponential factor(A) (min^{-1})	R^2
5	15.3093	0.3297	0.8861
15	15.7392	0.8949	0.8673
25	17.7969	2.9344	0.9162
30	17.6015	2.5497	0.8473

From the above table we can see that the Activation Energy increases with increasing heating rate and is in the range of 15.3093 – 17.6015 KJ/mol and the pre-exponential factor is in the range of

0.3297-2.5497 min⁻¹. The activation energy obtained is in close agreement with the value obtained by V. Volli *et al*[20] who calculated the Activation energy of different de-oiled cakes at different heating rates. The Activation energy for the neem de-oiled cake was 14.79, 15.46 and 17.79 KJ/mol for a heating rate of 10, 20, 30 °C/min.

5.5.2 Kissinger method

In the Kissinger method the Activation energy (E) and the pre-exponential factor (A) were calculated from equation (3). In the equation the maximum temperature, T_m corresponds to the temperature of maximum weight loss. These peak temperatures can be obtained from fig. 5.4. The plot of $\ln\left(\frac{\beta}{T_m^2}\right)$ versus 1000/T_m K⁻¹ is shown in fig.4. The regression equation and the square of the correlation coefficient is also presented. The Activation energy (E) and the pre-exponential factor (A) is calculated from the slope and intercept of the regression equation of the plot. The Activation energy (E) and the pre-exponential factor (A) obtained from the Kissinger method are 45.939 KJ/mol and 0.72156 min⁻¹.

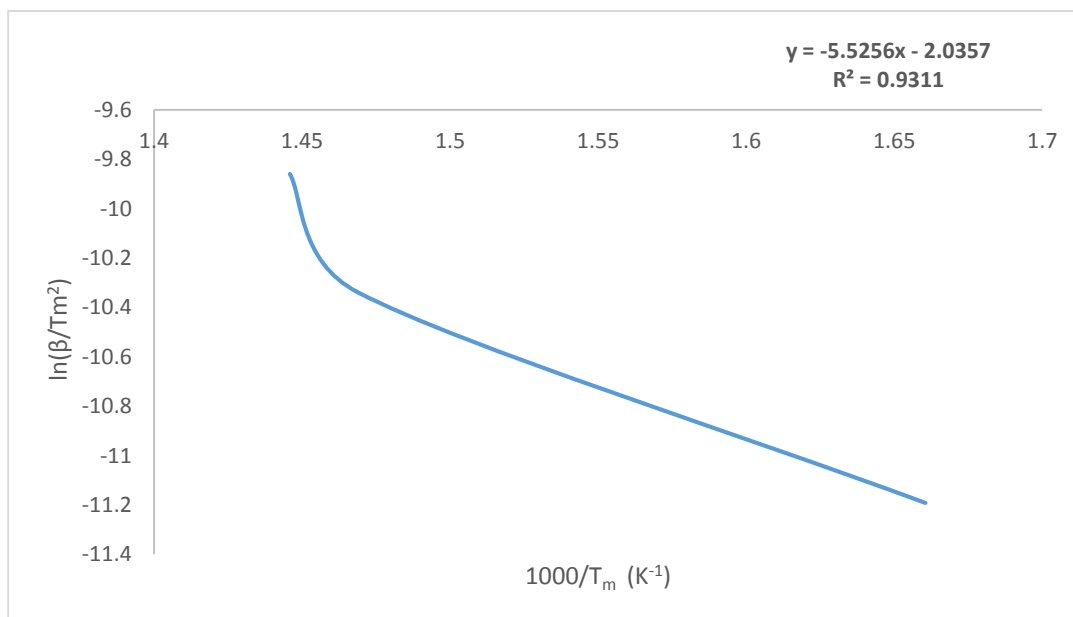


Fig.5.6 Kissinger plot of simal cotton seed

The kinetic parameters were obtained from FWO and KAS method using equation (5) and equation (9) for a given value of conversion (α). Figure 5.7 shows the plot of conversion versus temperature at four different heating rates. To calculate the kinetic parameters we chose a particular value of conversion, then at that value of conversion we found the corresponding temperatures for different heating rates. We have done the same thing for different values of conversion ranging from 0.4 to 0.8.

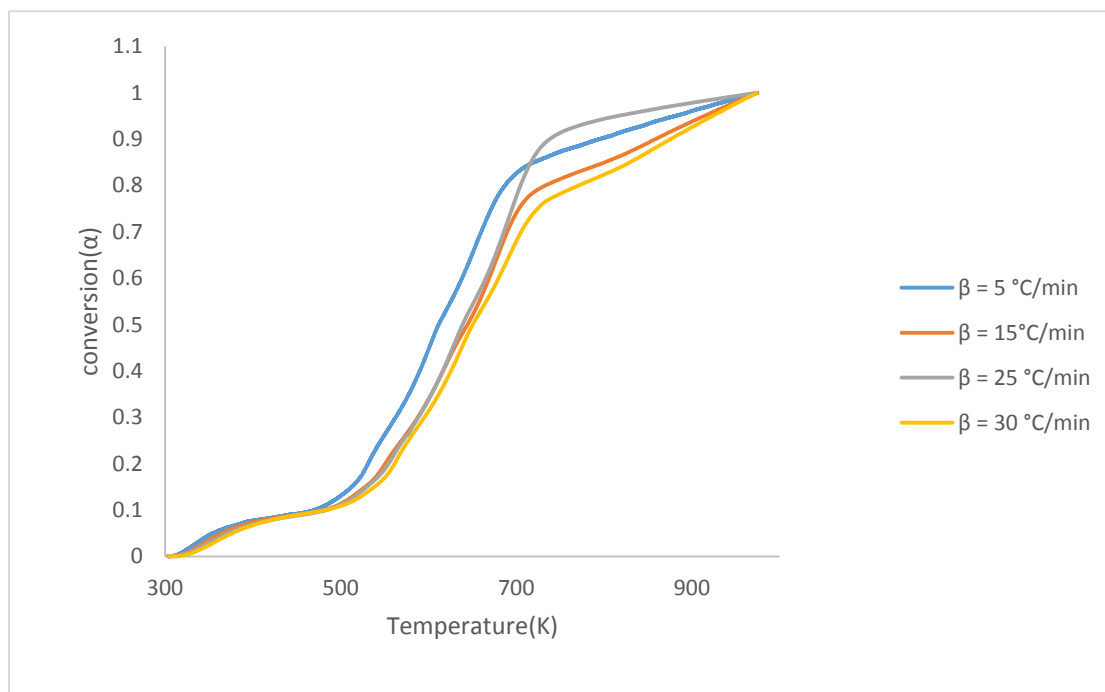


Fig.5.7 plot of conversion versus temperature at four different heating rates.

5.5.3 FWO and KAS method

The FWO plot of $\log \beta_i$ versus $1000/T_{\alpha, i} \text{ K}^{-1}$ for different values of conversion is shown in figure 5.8 and the KAS plot of $\log (\beta_i/T_{\alpha, i}^2)$ versus $1000/T_{\alpha, i} \text{ K}^{-1}$ for different values of conversion is shown in figure 5.9. The activation energies were obtained from the slope and the pre-exponential factors were obtained from the intercepts of the regression equations and are given in table 5.6.

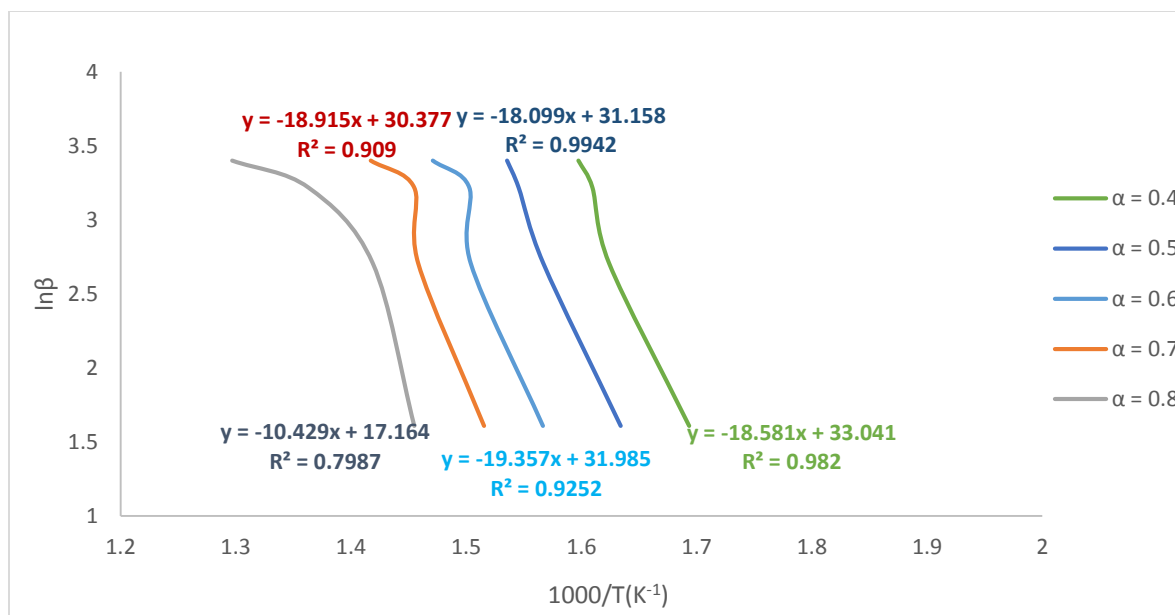


Fig.5.8 FWO plot of simal cotton seed for different values of conversion.

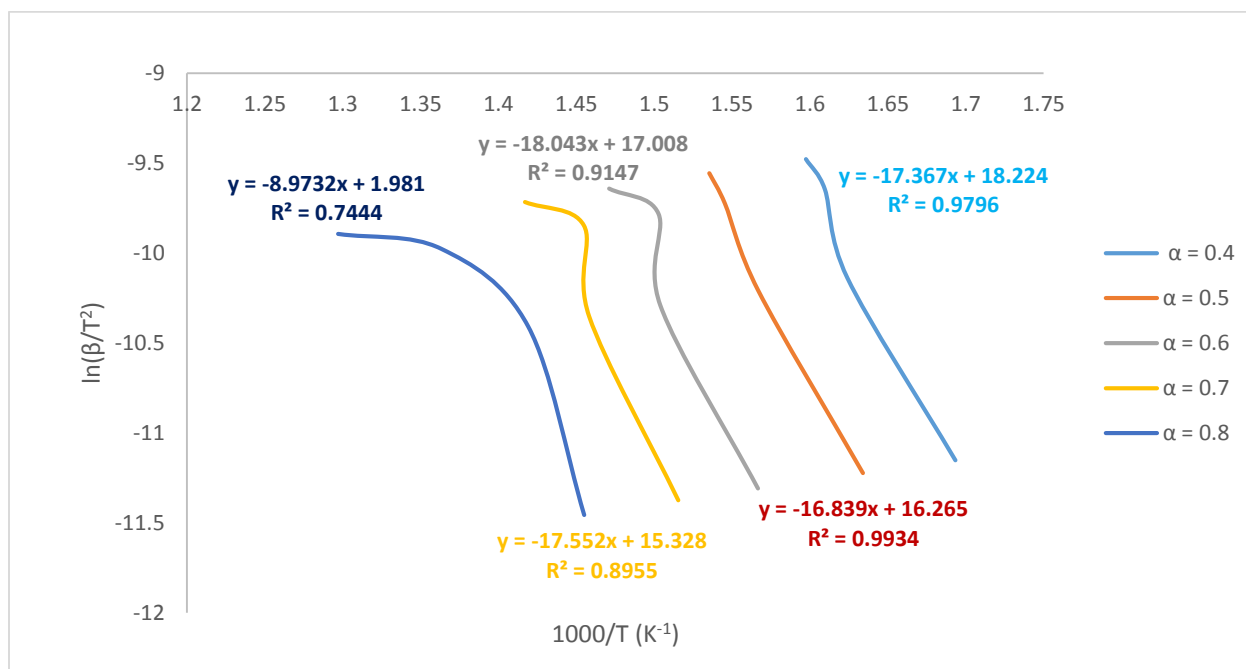


Fig.5.9 KAS plot of simal cotton seed (Bombax malabarica) for different values of conversion.

Table 5.6

Values of E, A and R² for simal cotton seed (*Bombax malabarica*) by FWO and KAS method

	FWO			KAS		
α	E (KJ/mol)	A (min ⁻¹)	R ²	E (KJ/mol)	A (min ⁻¹)	R ²
0.4	146.8464	1.3358x10 ¹²	0.9820	144.3892	7.2875x10 ¹¹	0.9796
0.5	143.0371	2.8324x10 ¹¹	0.9942	139.999	1.3518x10 ¹¹	0.9934
0.6	152.9791	8.0047x10 ¹¹	0.9252	150.0095	4.0255x10 ¹¹	0.9147
0.7	149.4860	2.1558x10 ¹¹	0.9090	145.9273	9.5897x10 ¹⁰	0.8955
0.8	82.4208	9.5477x10 ⁵	0.7987	74.6031	10.4702x10 ⁴	0.7444
Average	134.9538	5.2715x10 ¹¹		130.9856	2.7247x10 ¹¹	

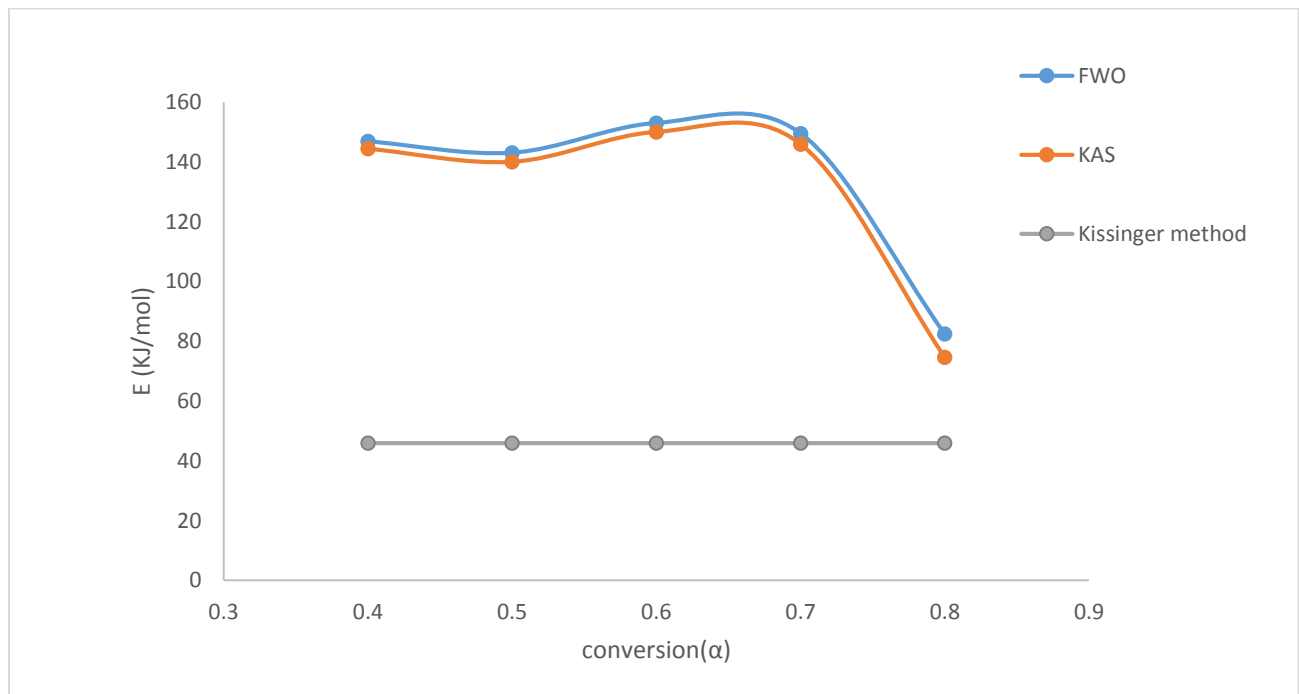


Fig.5.10 Activation energy (E) versus conversion (α)

Figure 5.10 shows the change of activation energy with conversion for the pyrolysis of simal cotton seed (*Bombax malabarica*). We can see that the activation energy obtained from FWO and KAS method is not same for all conversion. For FWO method, it ranges from 82.4208 to 152.9791 KJ/mol and for KAS method it ranges from 74.6031 to 150.0095 KJ/mol. It shows that the reaction mechanism is not same throughout the decomposition process and the activation energy depends on conversion.

5.6 Characterization of pyrolytic oil

5.6.1 Physical Characterization

Table 5.7

Physical properties of pyrolytic oil

Physical property	pyrolytic oil	diesel
Maximum yield	58.06 % by weight	
Temperature of maximum yield	600°C	
Appearance	Dark brown free flowing liquid	Yellowish
Odour	Smoky smell	Aromatic
Density at 15°C (gm/cc)	1.0168	0.85
Specific gravity at 15°C /15°C	1.0168	0.85
Kinematic viscosity at 50°C (CST)	69.15	2.5
Flash point in °C	31°C	76°C
Fire point in °C	40°C	-
Gross calorific value in Kcal/kg	6678.5416	10700
Miscibility	Methanol, Ethanol	

5.6.2 Chemical Characterization

5.6.2.1 GC-MS

The result obtained from the GC-MS analysis is shown in table 5.8 below and table 5.9 shows the structure of some major compounds. The name of the compound present in the bio oil and its area percentage is given in the table. From the area percentage we say that the major component present in the bio oil is 9, 12-Octadecadienoic acid (Z, Z) also known as linoleic acid with area percentage of 14.88%. It is a polyunsaturated omega-6 fatty acid. It is generally used in making quick-drying oil, useful for making oil paints and varnishes. The second major component is 10-undecenoic acid common name undecylenic acid with area percentage of 10.67%. It is also an organic unsaturated fatty acid. It is used in manufacture of pharmaceuticals, cosmetics and perfumery. The third compound present in abundance is 2-methylbutanal which is an aldehyde having an area % of 9.61. It is basically used in cocoa, coffee, wine and nuts for life. So we can see that the pyrolytic oil mainly consists of unsaturated fatty acids and aldehydes followed by saturated and unsaturated aliphatic hydrocarbons and very little aromatic compounds. Name and structure of some major compounds is given in table 5.9.

Table 5.8

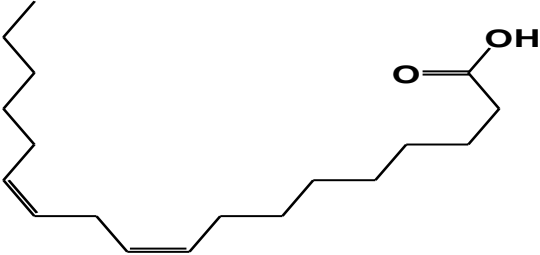
GC-MS of the liquid product

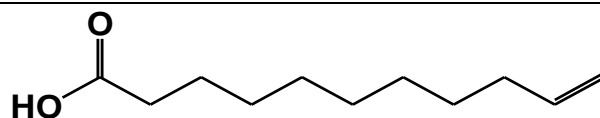
S.no.	R. Time (min)	Name of compound	Area (%)	Molecular formula
1.	1.399	2-methyl butanal	9.61	C ₅ H ₁₀ O
2.	1.667	n-heptane	1.65	C ₇ H ₁₆
3.	2.060	Toluene	1.55	C ₇ H ₈
4.	2.253	n-octane	1.71	C ₈ H ₁₈
5.	3.271	n-nonane	2.35	C ₉ H ₂₀
6.	4.408	Phenol	0.60	C ₆ H ₆ O
7.	4.556	Octan-2-one	2.33	C ₈ H ₁₆ O
8.	5.804	Benzene methanol	0.82	C ₇ H ₈ O
9.	6.064	n-1-undecene	2.15	C ₁₁ H ₂₂

10.	7.104	pentylbenzene	1.22	C ₁₁ H ₁₇
11.	7.558	1-dodecene	2.08	C ₁₂ H ₂₄
12.	8.598	Bicyclo[6.4.0]dodeca-9,11-diene	3.00	C ₁₂ H ₁₈
13.	9.118	Indole	0.84	C ₈ H ₇ N
14.	10.276	2,5-dimethyl-4-aminopyridine-N-oxide	3.99	C ₇ H ₁₀ N ₂ O
15.	11.651	10-undecenoic acid	10.67	C ₁₁ H ₂₀ O ₂
16.	12.609	6-butyl-1-nitro-1-cyclohexene	1.59	C ₁₀ H ₁₇ NO ₂
17.	12.698	Fucose, cyclic ethylene mercaptal	2.63	C ₆ H ₁₂ O ₅
18.	13.916	Heptadec-8-ene	7.77	C ₁₇ H ₃₄
19.	14.355	6(Z),9(E)-heptadecadiene	2.27	C ₁₇ H ₃₂
20.	14.986	Undecylbenzene	1.74	C ₁₇ H ₂₈
21.	16.219	Pentadecanenitrile	0.65	C ₁₅ H ₂₉ N
22.	16873	Hexadecanoic acid	2.09	C ₁₆ H ₃₂ O ₂
23.	17.906	13-Hexyloxacyclotridec-10-en-2-one	2.93	C ₁₈ H ₃₂ O ₂
24.	18.069	Oleanitrile	8.94	C ₁₈ H ₃₃ N
25.	18.678	9,12-Octadecadienoic acid (Z,Z)	14.88	C ₁₆ H ₃₂ O ₂
26.	19.800	2,5-dimethyl-3-propylpyrazine	3.07	C ₉ H ₁₄ N ₂

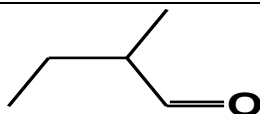
Table 5.9

Structure of some major compounds present in pyrolytic oil

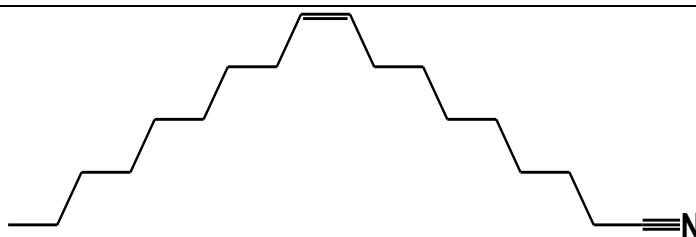
IUPAC name and Structure of compounds
 <p data-bbox="532 1722 1123 1753">(9Z,12Z)-9,12-Octadecadienoic acid</p>



10-undecenoic acid



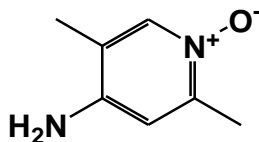
2-methylbutanal



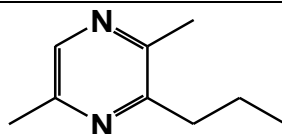
(9Z)-9-Octadecenitrile



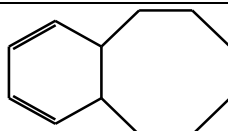
heptadec-8-ene



2,5-dimethyl-4-aminopyridine-N-oxide



2,5-dimethyl-3-propylpyrazine



bicyclo[6.4.0]dodeca-9,11-diene

5.6.2.2 FTIR Analysis

The infra-red spectra of the liquid product obtained using FTIR has been shown in figure 5.11. The frequencies obtained from the spectra have been compared against reference charts and the interpretation of the results have been shown in table 5.10. We can see that the result obtained from FTIR is in comparison with the result obtained from GC/MS. For eg.- From FTIR we observe that carboxylic group is present in the pyrolytic oil which is also confirmed by the GC/MS analysis.

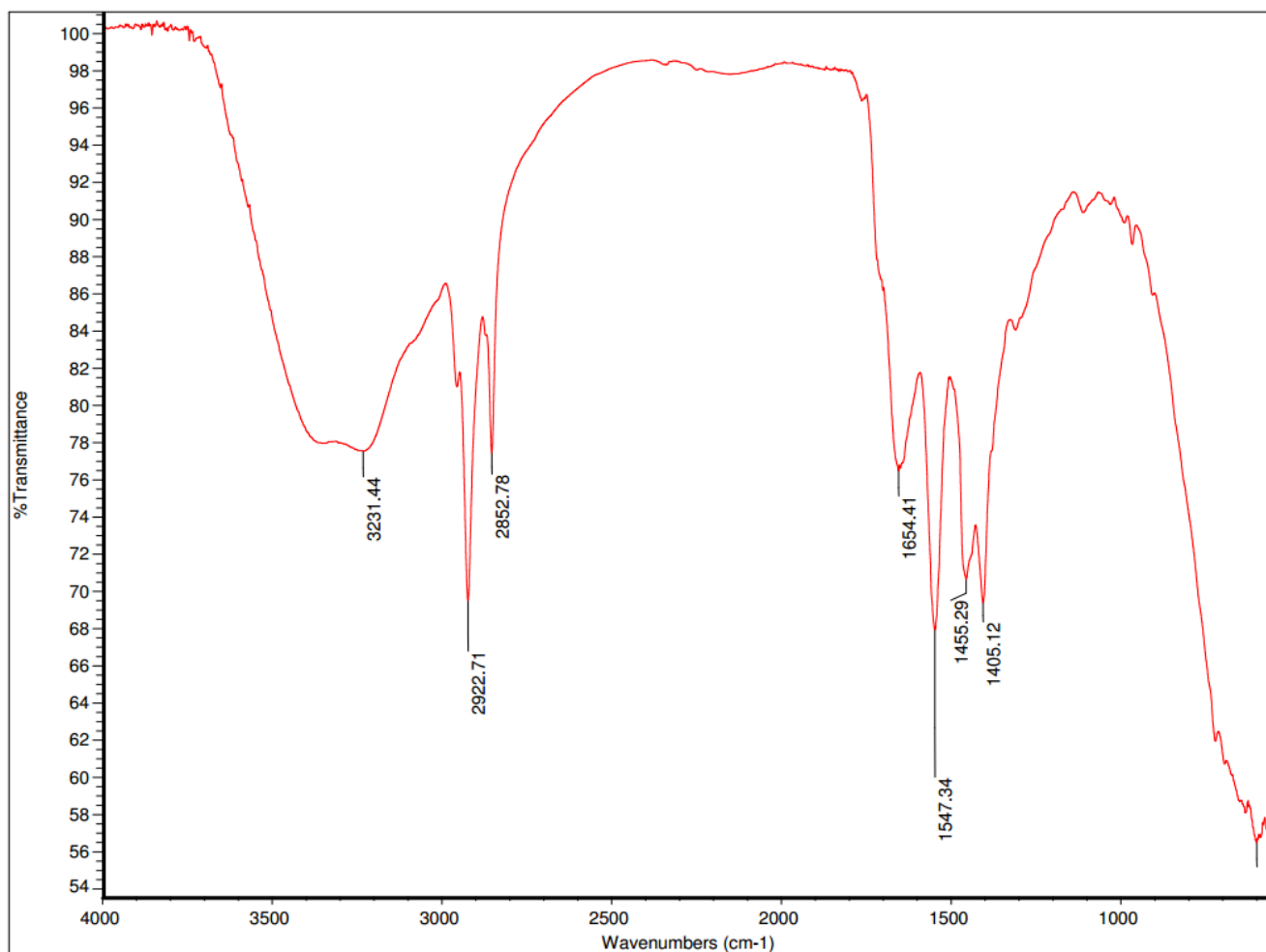


Fig. 5.11 IR spectra of the liquid product

Table 5.10**FTIR compound and frequency table**

Compound Type	Frequency (cm⁻¹)
H-Bonded Phenols	3231.44
C-H stretch Alkanes	2922.71
C-H stretch Alkanes	2852.78
C=C stretch Alkene	1654.41
N-O asymmetrical stretch Nitro compound	1547.34
Aromatic C-C stretch	1455.29
C-O stretch carboxylic acid	1405.12

5.7 Characterization of pyrolytic char**5.7.1 Proximate Analysis of pyrolytic char**

Table 5.10 shows the result for proximate analysis of simal cotton seed.

Table 5.10**Proximate Analysis of pyrolytic char**

Proximate Analysis of pyrolytic char	
Moisture (%)	3.6
Volatile matter (%)	16.5
Ash (%)	26.3
Fixed carbon (%)	53.6

Proximate analysis of pyrolytic char shows that even after pyrolysis some volatile matter was present in the char which means the pyrolysis was done completely.

5.7.2 Calorific Value of pyrolytic char

The calorific value of char obtained from pyrolysis of simal cotton seed was found to be 5158.9338 Kcal/Kg. So the char can be used as a solid fuel.

5.7.3 SEM of char

SEM analysis was done using JSM-6480LV Scanning Electron Microscope. The SEM photographs of the pyrolytic char at different magnification of 250X, 500X and 1000X are shown in figure 5.12, 5.13 and 5.14. From the photographs we can see that the char has a porous structure. So it can be used as an adsorbent as activated carbon.

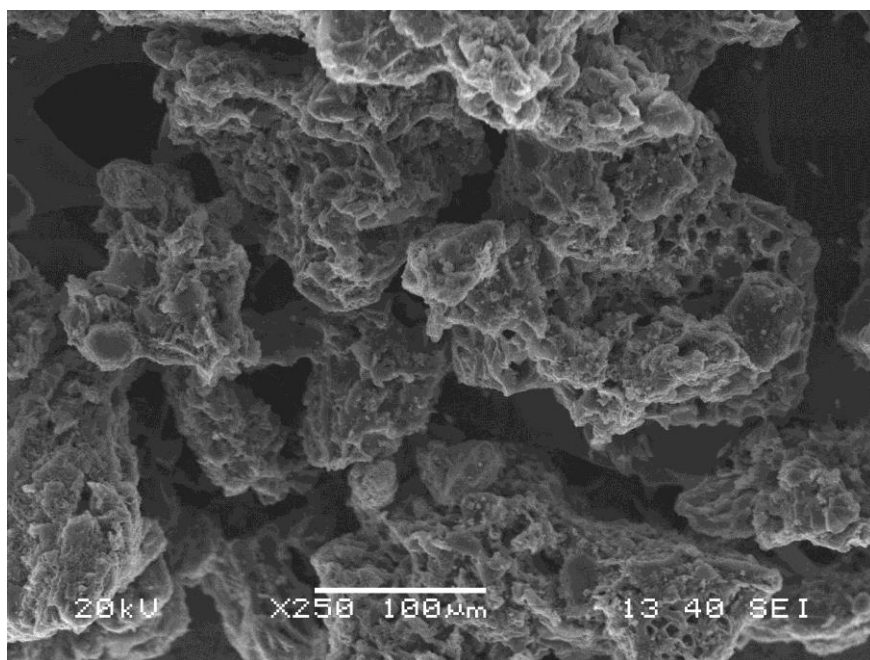


Fig 5.12 Simal cotton seed char at 250X magnification

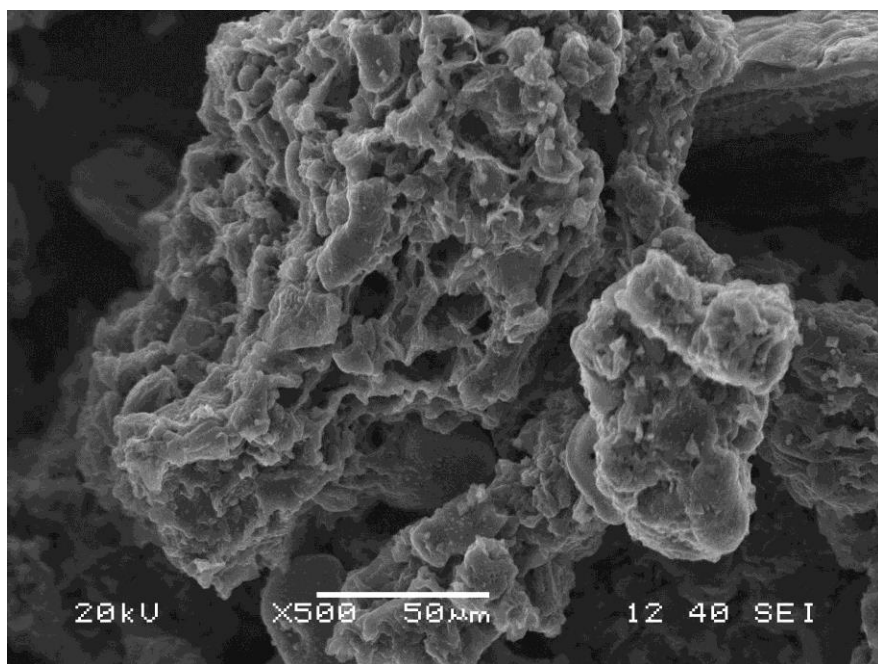


Fig 5.13 Simal cotton seed char at 500X magnification

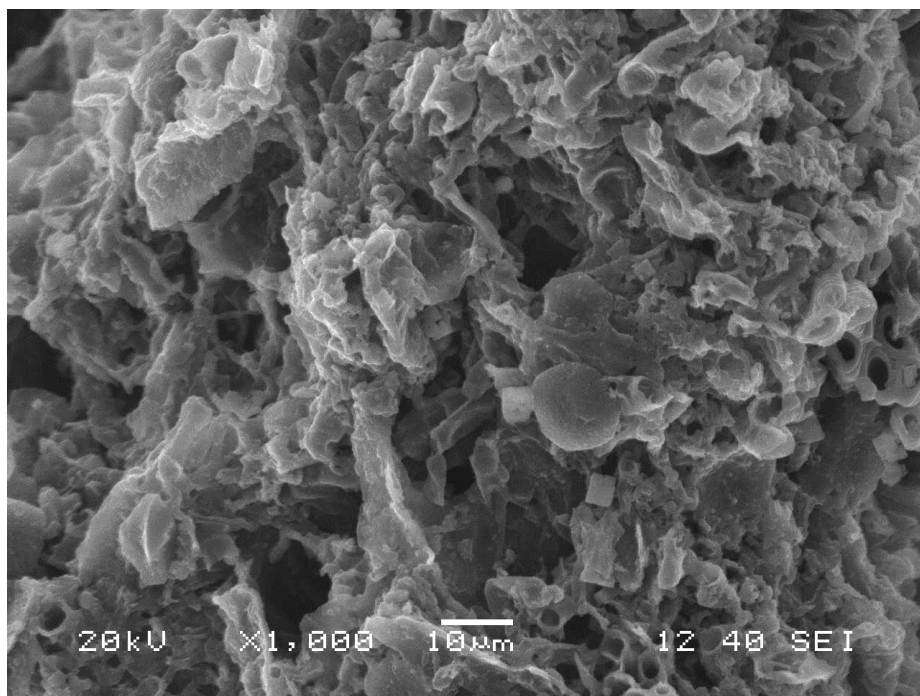


Fig 5.14 Simal cotton seed char at 1000X magnification

Chapter 6

(CONCLUSION)

In this work, pyrolysis experiments were done on simal cotton seed in a semi batch reactor in a temperature range of 450-700°C and at a heating rate of 20°C min⁻¹. The following conclusions were drawn:

- The maximum yield of bio-oil was obtained to be 58.06% at a temperature of 600°C which is known as optimum temperature.
- Liquid yield increases with increases in temperature, becomes maximum at an optimum temperature of 600°C and then decreases because of cracking of vapor after 600°C. Char yield decreases with increases in temperature reaches a minimum at optimum temperature and then increases. Gases yield increases initially and then decreases.
- Liquid yield increases with decrease in feed size, char yield and the gases yield decreases.

This shows that the temperature and feed size has significant effect on the product yield.

- Calorific value was found to be 6678.5416Kcal/kg which is around 62.37% of diesel oil.
- GC-MS analysis showed that around 26 compounds are present in the pyrolytic oil. The major component were 9, 12-Octadecadienoic acid (Z, Z) also known as linoleic acid, 10-undecenoic acid, 2-methyl butanal, heptadec-8-ene and other aldehydes, ketones, saturated and unsaturated aliphatic hydrocarbons and some aromatic compounds. Separation and analysis of these compounds can lead to major industrial applications.
- FTIR analysis showed the presence of carboxylic acids and phenols along with different straight chain alkanes and alkenes.

Chemical characterization of the pyrolytic oil showed that it can be used as a synthetic fuel.

- Proximate analysis of the pyrolytic char and its calorific value which was found to be 5158.9338 Kcal/kg showed that it can be used as a solid fuel.
- SEM-EDX of the char showed that it can be used as an adsorbent.

Following conclusions were drawn from kinetic study of simal cotton seed:

- From the results obtained from Coat and redfern method we can say that the Activation Energy is a function of heating rate and it increases with increasing heating rate.
- In Kissinger method we observed the kinetic parameters do not change throughout the decomposition process.

- In FWO and KAS method the kinetic parameters varied with conversion value.
- The activation energies obtained from the two methods of FWO and KAS are almost analogous. We can say that the Kissinger method is not suitable for the calculation of kinetic parameters of the given sample while the value of the kinetic parameters obtained from the isoconversional methods of FWO and KAS are in good agreement with the literature. The result showed that the model-free method satisfactorily described the complexity of the pyrolysis process but for detailed study of the process further analysis is required.

Future work

The yield of the oil obtained from pyrolysis of simal cotton seed can be improved by using different methods like varying the reaction conditions, using different type of reactors etc. Also the oil quality can be improved by using different methods of upgradation like hydrocracking, hydro-treating, solvent addition/esterification, and emulsification. Pyrolysis can also be done in the presence of various catalysts to improve the quality of bio-oil obtained.

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